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European Patent Office
Office européen des brevets



⑪ Publication number:

0 649 820 A1

⑫

EUROPEAN PATENT APPLICATION
published in accordance with Art.
158(3) EPC

⑬ Application number: 93914940.7

⑭ Int. Cl. 5: C02F 11/14, B01D 21/01

⑮ Date of filing: 30.06.93

⑯ International application number:
PCT/JP93/00904

⑰ International publication number:
WO 94/01370 (20.01.94 94/03)

⑲ Priority: 04.07.92 JP 200624/92

⑳ Date of publication of application:
26.04.95 Bulletin 95/17

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DE FR

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㉕ SLUDGE DEHYDRATING AGENT.

EP 0 649 820 A1

㉖ A sludge dehydrating agent which is excellent in storage stability and prevented from becoming water-insoluble during storage and hence can be distributed in the market securely by solving the problem of the conventional dehydrating agents comprising amphoteric polymers that they undergo deterioration and become water-insoluble when stored for long, thus becoming substantially unusable. This dehydrating agent comprises a copolymer composed of cationic vinyl monomer units, vinylic carboxylic acid monomer units and nonionic vinyl monomer units and a salt of a group IIA metal of the periodic table. Preferable examples of the vinylic carboxylic acid monomer include acrylic, methacrylic and crotonic acids, while those of the nonionic vinyl monomer include acrylamide and methacrylamide. The metal salts usable herein include those of mineral acids and organic carboxylic acids, and preferable mineral acid salts include calcium chloride, magnesium chloride and magnesium sulfate. Preferably, the amount of the cationic vinyl monomer ranges from 10 to 60 mole %, while that of the vinylic carboxylic acid monomer from 10 to 45 mole %. Preferably, the molar ratio of the cationic vinyl monomer to the vinylic carboxylic acid monomer ranges from 0.3 to 3.0, while that of the metal salt to the carboxylic acid monomer from 0.2 to 2.0. The dehydrating agent may further contain an inorganic coagulant.

Technical Field

The present invention relates to a sludge dehydrating agent comprising amphoteric polymers, and more particularly to a sludge dehydrating agent comprising amphoteric polymers, which is excellent in storage stability undergoing little deterioration with time.

Background Art

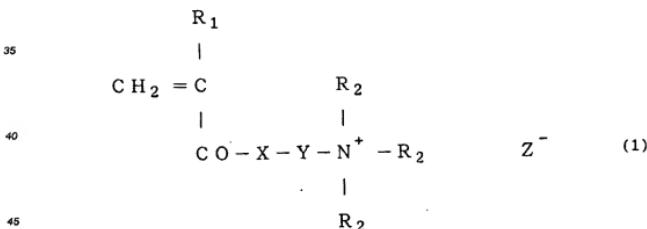
Previously dehydrating agents comprising cationic polymers have been known as sludge dehydrating agents. However, conventional dehydrating agents are becoming unsatisfactory in performance because of the recent worsening and diversification in sludge properties and, therefore, an improvement in the performance thereof has been sought. In this connection, sludge dehydrating agents having strong aggregation force and comprising amphoteric polymers have been proposed which are superior in recovery of suspended substances, water content of cake and release of cake from filter cloth. However, conventional sludge dehydrating agents comprising amphoteric polymers had a disadvantage that they undergo deterioration during storage and become water-insoluble while being used. In order to solve this problem, JP-A-3-293100 proposed a sludge dehydrating agent having an improved storage stability by further adding a specific cationic monomer onto an amphoteric polymer comprising a specific cationic monomer, an anionic monomer and a nonionic monomer. With this improved agent, however, the shelf life is not long enough and hence cannot be distributed securely in the market.

The object of the present invention is to provide a sludge dehydrating agent which is excellent in storage stability without becoming water-insoluble during storage by the improvement of conventional sludge dehydrating agents comprising amphoteric polymers.

Disclosure of Invention

In order to attain the object described above, the present invention uses a sludge dehydrating agent comprising a copolymer composed of cationic vinyl monomer units, vinylic carboxylic acid monomer units and nonionic vinyl monomer units and a salt of a group IIA metal of the periodic table.

In the sludge dehydrating agent of the invention it is preferable to use as the cationic vinyl monomer the following compound expressed by the general formula (1).



, wherein

- 50 R_1 denotes a hydrogen atom or a methyl group,
 R_2 denotes a hydrogen atom, a methyl group an ethyl group or a benzyl group,
 X denotes O or NH
 Y denotes $CH_2 CH_2$, $CH_2 CH_2 CH_2$ or $CH_2 CH(OH)CH_2$,
 Z denotes a chlorine atom, a bromine atom, an iodine atom, a sulfate group, or a methyl sulfate group.

Preferable examples of the vinylic carboxylic acid monomer include acrylic acid, methacrylic acid or crotonic acid, while those of the nonionic vinyl monomer include acrylamide or methacrylamide. The metal salts used may be those of mineral acid or organic carboxylic acids, and preferable mineral acid salts

include calcium chloride, magnesium chloride or magnesium sulfate.

In the sludge dehydrating agent described above the amount of the cationic vinyl monomer is preferably in the range from 10 to 60 mole %, while the amount of the vinylic carboxylic acid monomer is preferably in the range from 10 to 45 mole %. The molar ratio of the cationic vinyl monomer to the vinylic carboxylic acid monomer is preferably in the range from 0.3 to 3.0, and the content of the salt of a group IIA metal based on the molar ratio to the vinylic carboxylic acid monomer may be preferably in the range from 0.2 to 2.0. Further, an inorganic coagulant can be added to the sludge dehydrating agent of the invention.

10 The Best Mode for Carrying Out the Invention

The sludge dehydrating agent of the invention is characterized in that a sludge dehydrating agent which comprises a copolymer having cationic vinyl monomer units, vinylic carboxylic acid monomer units and nonionic vinyl monomer units, which will be hereafter designated "Copolymer A", is added with a salt of a group IIA metal of the periodic table.

15 First, the compounds used in the sludge dehydrating agent of the invention will be explained.

Typical examples of the cationic vinyl monomer are (meth)acryloyloxy(hydroxy)alkyl quaternary or tertiary ammonium salts and (meth)acrylamido(hydroxy)alkyl quaternary or tertiary ammonium salts. Examples of (meth)acryloyloxy(hydroxy)alkyl quaternary or tertiary ammonium salts are acryloyloxyethyltrimethylammonium chloride, methacryloyloxyethyltrimethylammonium chloride, acryloyloxyethyltrimethylammonium bromide, methacryloyloxyethyltrimethylammonium chloride, methacryloyloxy(hydroxy)propyltrimethylammonium chloride, methacryloyloxyethyltrimethylammonium methosulfate, methacryloyloxyethyltrimethylammonium bromide, methacryloyloxyethyltrimethylammonium iodide, and methacryloyloxyethyltrimethylammonium chloride. Examples of (meth)acrylamido(hydroxy)alkyl quaternary or tertiary ammonium salts are acrylamidepropyltrimethylammonium chloride, acrylamidepropyltrimethylammonium sulfate, and methacrylamidepropyltrimethylammonium sulfate. Among these compounds the cationic vinyl monomers as expressed by the general formula (1) are preferably used.

20 Typical examples of the vinylic carboxylic acid monomers are acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, itaconic acid, maleic acid, and fumaric acid. Preferable among these are acrylic acid, methacrylic acid and crotonic acid.

25 Examples of the nonionic vinyl monomers are water soluble nonionic monomers, preferably acrylamide and methacrylamide. A small amount of a hydrophobic nonionic vinyl monomer may be used in combination, unless Copolymer A becomes insoluble in water.

In Copolymer A the amount of the cationic vinyl monomer is usually in the range from 10 to 60 mole %, preferably from 20 to 45 mole %. When the amount of the cationic vinyl monomer is smaller than 10 %, water content of the cake becomes not sufficient in using the sludge dehydrating agent of the invention; while, when the amount thereof exceeds 60 mole %, strong aggregation force which is characteristic of an amphoteric polymer is not obtained. The amount of the vinylic carboxylic acid monomer in Copolymer A is usually in the range from 10 to 45 mole %, preferably from 20 to 40 mole %. When the amount of the vinylic carboxylic acid monomer is smaller than 10 %, strong aggregation force which is characteristic of an amphoteric polymer is not obtained in using the sludge dehydrating agent of the invention, and on the other side, when the amount thereof exceeds 45 mole %, water content of the cake becomes not sufficient.

30 The molar ratio of the cationic vinyl monomer to the vinylic carboxylic acid monomer in Copolymer A is usually in the range from 0.3 to 3.0 based on the amount of the vinylic carboxylic acid monomer to the cationic vinyl monomer, preferably from 0.5 to 2.0. When the ratio is smaller than 0.3, water content and releasing ability from filter cloth of the cake are not sufficient in using the sludge dehydrating agent of the invention and, when the molar ratio exceeds 3.0, strong aggregation force which is characteristic of an amphoteric polymer is not obtained.

35 The amount of the nonionic vinyl polymer in Copolymer A is usually in the range from 5 to 80 mole %, preferably from 10 to 60 mole %. When the amount of the nonionic vinyl monomer is smaller than 5 mole %, strong flocculating power which is characteristic of an amphoteric polymer is not obtained in using the sludge dehydrating agent of the invention and, when the amount thereof exceeds 80 %, water content of the cake becomes not sufficient.

40 Examples of the salts of group IIA metals include mineral acid salts of group IIA metals, such as calcium chloride, magnesium chloride, magnesium sulfate, calcium nitrate and strontium chloride, and organic acid salts of group IIA metals, such as calcium acetate and magnesium lactate. Preferable among these salts are calcium chloride, magnesium chloride and magnesium sulfate.

The amount of the salts of group IIA metals is in the range from 0.2 to 2.0 by the molar ratio of the salt to the vinylic carboxylic acid monomer, preferably from 0.3 to 1.0. When the molar ratio of the salt of a group IIA metal to the vinylic carboxylic acid monomer is smaller than 0.2, long-term storage stability of the sludge dehydrating agent is not sufficient, while the molar ratio exceeding 2.0 is not preferable because of the decrease in the amount of active ingredients of the sludge dehydrating agent.

5 The intrinsic viscosity of the sludge dehydrating agent of the invention as measured in a 1 N aqueous solution of NaNO_3 at 30 °C is at least not less than 3.0 dl/g, preferably not less than 4.0 dl/g. When the intrinsic viscosity is smaller than 3.0 dl/g, it is feared that the flocculating force is not sufficient, and therefore, some trouble in dehydration occurs, in using the sludge dehydrating agent of the invention.

10 In the following the process of preparing the sludge dehydrating agent of the invention will be explained in detail. In the preparation of the sludge dehydrating agent of the invention any of the known methods such as aqueous solution polymerization, emulsion polymerization and suspension polymerization can be employed. For example, in case of carrying out a aqueous solution polymerization, a polymerization catalyst is added to an aqueous solution of monomers of the concentration of 10 to 80 % by weight, contained in a reactor which is purged of the air by passage of an inert gas, and then the monomers are polymerized at 20 to 100 °C for a few hours. Examples of the polymerization catalyst used are persulfates such as ammonium persulfate and potassium persulfate, organic peroxides such as benzoyl peroxide, azoic compounds such as 2,2'azobis(amidinopropane) hydrochloride and azobiscyanovaleic acid, and redox catalyst comprising combinations of peroxides such as hydrogen peroxide and potassium peroxide with reducing agents such as sodium bisulfite and ferrous sulfate.

20 More particularly, an ordinary polymerization may be carried out after dissolving preliminarily a salt of a group IIA metal or an aqueous solution thereof into an aqueous solution containing a certain amount of a cationic vinyl monomer, a vinylic carboxylic acid monomer and a nonionic vinyl monomer. Another method of carrying out the polymerization is that, into an aqueous solution containing a cationic vinyl monomer, a vinylic carboxylic acid monomer and a nonionic vinyl monomer is admixed a salt of a group IIA metal or an aqueous solution thereof, while the polymerization reaction of the monomers is proceeding or after the aqueous solution thereof, while the polymerization reaction of the monomers is proceeding or after the polymerization reaction has been completed. Still another method which can be taken is that the amphoteric polymer obtained by the polymerization of the above-mentioned monomers in an aqueous solution is dried and powdered, and impregnated thereafter with an aqueous solution of a salt of a group IIA metal.

30 The sludge dehydrating agent of the invention can be used independently or in combination with an inorganic coagulant such as polyaluminum chloride and ferric chloride. These inorganic coagulant agents can be admixed to the sludge dehydrating agent either before or after the sludge dehydrating agent is applied to the sludge.

35 The dosage of the sludge dehydrating agent of the invention to be added to the sludge is usually from 0.2 to 5 % by weight on the dry solids content of the sludge, preferably from 0.4 to 1.5% by weight. When the dosage is smaller than 0.2 % by weight on the dry solids content, the recovery of the suspended materials are not sufficient, while the dosage of more than 5 % by weight brings about an economic disadvantage.

40 In applying the sludge dehydrating agent of the invention, it can be added to the sludge either directly or after being admixed with water and dispersed, thereby being formed an aqueous solution. The sludge dehydrating agent is added to the sludge, stirred and mixed thereafter to form flocs. The flocs obtained are dehydrated by a dehydrator such as a belt press dehydrator.

45 The invention will be explained more fully by referring to the following description of the examples and the comparative examples. However, it is to be understood that the invention is not intended to be limited to the specific embodiments.

Example 1

An aqueous solution was prepared by mixing 0.30 mole of acryloyloxyethyltrimethylammonium chloride, 50 0.05 mole of methacryloyloxyethyltrimethylammonium chloride, 0.30 mole of acrylic acid, 0.35 mole of acrylamide, 0.09 mole of calcium chloride and 130 grams of water and, after purging the air by the passage of nitrogen, the solution was poured into a petridish of 30 cm internal diameter and 5 cm depth. Then 0.1 gram of ammonium persulfate was added to the solution and it was polymerized by keeping the temperature between 40 and 50 °C. The polymerization was started immediately and completed in about one hour. The polymer obtained was taken out, chopped into pieces and, after being dried at 100 °C in an oven until the solid content reaches 90 %, pulverized to obtain a powdery sludge dehydrating agent of the invention, which will be hereafter designated C-1.

The sludge dehydrating agent obtained was immediately stored in a thermostatic chamber kept at 40 °C, and was applied for the evaluation of the storage stability at three months, six months and nine months after starting the storage. The results of the evaluation are tabulated in Table 1. The evaluation of the storage stability was carried out by adding one gram of the sludge dehydrating agent sample carefully, into a 500 ml beaker containing 500 grams of distilled water by stirring with a jar tester, not to flocculate the sample, followed by stirring for two hours, and observing the solubility of the sample thereafter.

Example 2

10 An aqueous solution was prepared by mixing 0.30 mole of acryloyloxyethyltrimethylammonium chloride, 0.05 mole of methacryloyloxyethyltrimethylammonium chloride, 0.30 mole of acrylic acid, 0.35 mole of acrylamide, 0.30 mole of calcium chloride and 130 grams of water, followed by carrying out the same process as described in Example 1, to obtain the powdery sludge dehydrating agent of the invention, hereafter called C-2.

15 The sludge dehydrating agent obtained was evaluated by the same method as in Example 1. The results are tabulated in Table 1.

Example 3

20 An aqueous solution was prepared by mixing 0.35 mole of acryloyloxyethyltrimethylammonium chloride, 0.30 mole of acrylic acid, 0.35 mole of acrylamide, 0.15 mole of calcium chloride and 130 grams of water, followed by the same procedure as in Example 1, the powdery sludge dehydrating agent of the invention, hereafter called C-3, was obtained.

25 The sludge dehydrating agent obtained was evaluated by the same method as in Example 1. The results are tabulated in Table 1.

Example 4

An aqueous solution was prepared by mixing 0.10 mole of acryloyloxyethyltrimethylammonium chloride, 30 0.20 mole of acrylamidepropyltrimethylammonium chloride, 0.30 mole of acrylic acid, 0.35 mole of acrylamide, 0.15 mole of calcium chloride and 130 grams of water, followed by the same procedure as in Example 1, the powdery sludge dehydrating agent of the invention, hereafter called C-4, was obtained.

The sludge dehydrating agent obtained was evaluated by the same method as in Example 1. The results are tabulated in Table 1.

Example 5

An aqueous solution was prepared by mixing 0.30 mole of acryloyloxyethyltrimethylammonium chloride, 40 0.05 mole of methacryloyloxyethyltrimethylammonium chloride, 0.30 mole of acrylic acid, 0.35 mole of acrylamide, 0.30 mole of magnesium sulfate and 130 grams of water, followed by the same procedure as in Example 1, the powdery sludge dehydrating agent of the invention, hereafter called C-5, was obtained.

The sludge dehydrating agent obtained was evaluated by the same method as in Example 1. The results are tabulated in Table 1.

Example 6

An aqueous solution was prepared by mixing 0.35 mole of methacryloyloxyethyltrimethylammonium chloride, 50 0.05 mole of methyl sulfate, 0.30 mole of acrylic acid, 0.35 mole of acrylamide, 0.30 mole of calcium chloride and 130 grams of water, followed by the same procedure as in Example 1, the powdery sludge dehydrating agent of the invention, hereafter called C-6, was obtained.

The sludge dehydrating agent obtained was evaluated by the same method as in Example 1. The results are tabulated in Table 1.

Comparative Example 1

55 An aqueous solution was prepared by mixing 0.30 mole of acryloyloxyethyltrimethylammonium chloride, 0.05 mole of methacryloyloxyethyltrimethylammonium chloride, 0.30 mole of acrylic acid, 0.35 mole of acrylamide and 130 grams of water, followed by the same procedure as in Example 1, a powdery sludge

dehydrating agent, hereafter called C-7, was obtained.

The sludge dehydrating agent obtained was evaluated by the same method as in Example 1. The results are tabulated in Table 1.

5 Comparative Example 2

An aqueous solution was prepared by mixing 0.35 mole of acryloyloxyethyltrimethylammonium chloride, 0.30 mole of acrylic acid, 0.35 mole of acrylamide and 130 grams of water, followed by the same procedure as in Example 1, a powdery sludge dehydrating agent, hereafter called C-8, was obtained.

10 The sludge dehydrating agent obtained was evaluated by the same method as in Example 1. The results are tabulated in Table 1.

Comparative Example 3

15 An aqueous solution was prepared by mixing 0.30 mole of acryloyloxyethyltrimethylammonium chloride, 0.05 mole of methacryloyloxyethyltrimethylammonium chloride, 0.30 mole of acrylic acid, 0.35 mole of acrylamide, 0.30 mole of sodium chloride and 130 grams of water, followed by the same procedure as in Example 1, a powdery sludge dehydrating agent, hereafter called C-9, was obtained.

20 The sludge dehydrating agent obtained was evaluated by the same method as in Example 1. The results are tabulated in Table 1.

Comparative Example 4

25 An aqueous solution was prepared by mixing 0.35 mole of methacryloyloxyethyltrimethylammonium chloride, 0.65 mole of acrylamide, 0.30 mole of calcium chloride and 130 grams of water, followed by the same procedure as in Example 1, a powdery sludge dehydrating agent, hereafter called C-10, was obtained.

The sludge dehydrating agent obtained was evaluated by the same method as in Example 1. The results are tabulated in Table 1.

30

Table 1

Sludge Dehydrating Agent	After 3 Months	After 6 Months	After 9 Months
35	C-1	○	○
	C-2	○	○
	C-3	○	○
	C-4	○	○
	C-5	○	○
	C-6	○	○
40	C-7	○	X
	C-8	X	X
	C-9	○	X
	C-10	○	X
45 ○ : An aqueous solution forming a homogeneous liquid was produced.			
X : An aqueous solution containing an insoluble gel was produced.			

50 As apparent from the results shown in Table 1, all of the sludge dehydrating agents of the invention, C-1 ~ C-6, show no problem of insolubility by the deterioration during the storage time.

Application Example 1

55 The sludge dehydrating agent (C-6) of Example 6 and the sludge dehydrating agent (C-10) of Comparative Example 4 were evaluated by the suction filter test and the squeeze test by using mixed sludge from a sewage disposal plant (pH5.6, suspended matter 1.9 wt/vol %). The procedure is as follows.

5 Into a 300 ml beaker was taken 200 ml of sludge, and then was added a required amount of a 0.3 % by weight of an aqueous solution of sludge dehydrating agent, followed by stirring at 200 rpm for 30 seconds using a turbine impeller mixer, to be produced flocs of the sludge. The diameter of the flocs produced was then measured. Next, onto a suction filter covered with a nylon filter cloth was placed a cylindrical tube of 5 cm internal diameter, and then the flocculated sludge was poured into the tube, whereby the amount of the filtrate during 10 seconds was measured. Recovery of the suspended matter was calculated by measuring the amount of the suspended matter in the filtrate. Furthermore, a certain amount of the sludge filtrated was sandwiched between two filter cloths for belting press, then squeezed at a pressure of 0.5 Kg/cm² for 60 seconds, whereby the releasing ability from the filter cloth and the water content of the dehydrated cake 10 were measured. The results of these tests are tabulated in Table 2.

Table 2

15	Sludge Dehydrating Agent	C-6			C-10		
		100	130	160	100	130	160
16	Amount Added(ppm)	3	5	6	3	4	5
17	Floc Diameter(mm)	120	142	148	88	102	120
18	Amount of Filtrate during 10 sec(ml)	99<	99<	99<	89	92	94
19	Recovery of Suspended Matter(%)	○	○	○	X	△	○
20	Release property from Filter Cloth	78.5	76.8	76.2	83.1	81.8	80.1
	Water Content of Dehydrated Cake(%)	○ :Good △ :Poor X : Bad					

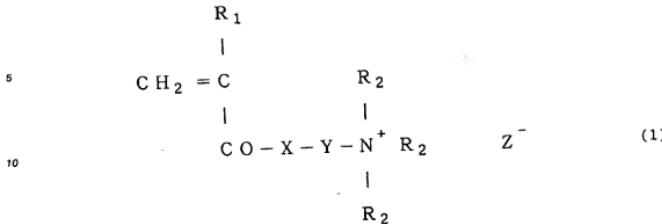
25 As apparent from the suction filter test and the squeeze test, the sludge dehydrating agent of the invention has a superior effect for the sludge dehydration as compared with the cationic polymer sludge dehydrating agents usually used for the sludge dehydration.

Industrial Applicability

30 The sludge dehydrating agent of the invention show no problem, unlike conventional sludge dehydrating agents, of insolubility by the deterioration, to be substantially unusable when stored for a long time, and hence it can be distributed in the market securely. The sludge dehydrating agent of the invention can be, therefore, used for the dehydration of the organic sludges including the live sludge such as sewage, excrement, factory waste water or the like, the activated excess sludge, the digested sludge, the flocculated sludge, or the mixed sludge thereof, which are discharged from sewage, excrement, factory waste water treatment plants or the like.

Claims

- 40 1. A sludge dehydrating agent comprising a copolymer composed of cationic vinyl monomer units, vinylidic carboxylic acid monomer units and nonionic vinyl monomer units and a salt of a group IIA metal of the periodic table.
- 45 2. A sludge dehydrating agent of claim 1 wherein the cationic vinyl monomer is a compound expressed by the general formula (1),



- 15 , wherein
- 20 R_1 denotes a hydrogen atom or a methyl group,
 R_2 denotes a hydrogen atom, a methyl group, an ethyl group or a benzyl group,
 X denotes O or NH,
 Y denotes CH_2 CH_2 , CH_2 CH_2 CH_2 or CH_2 $\text{CH}(\text{OH})\text{CH}_2$,
and
 Z denotes a chlorine atom, a bromine atom, an iodine atom, a sulfate group, or a methyl sulfate group.
- 25 3. A sludge dehydrating agent of claim 1 wherein the vinylic carboxylic acid monomer is acrylic acid, methacrylic acid or crotonic acid.
- 30 4. A sludge dehydrating agent of claim 1 wherein the nonionic-vinyl monomer is acrylamide or methacrylamide.
- 35 5. A sludge dehydrating agent of claim 1 wherein the salt of a group IIA metal is a salt of a mineral acid or a salt of an organic carboxylic acid.
- 40 6. A sludge dehydrating agent of claim 5 wherein the salt of a mineral acid is calcium chloride, magnesium chloride or magnesium sulfate.
- 45 7. A sludge dehydrating agent of claim 1 wherein the amount of the cationic vinyl monomer is from 10 to 60 mole %.
8. A sludge dehydrating agent of claim 1 wherein the amount of the vinylic carboxylic acid monomer is from 10 to 45 mole %.
9. A sludge dehydrating agent of claim 1 wherein the molar ratio of the cationic vinyl monomer to the vinylic carboxylic acid monomer is in the range from 0.3 to 3.0.
- 50 10. A sludge dehydrating agent of claim 1 wherein the content of the salt of a group IIA metal is in the range from 0.2 to 2.0 as expressed by the molar ratio to the vinylic carboxylic acid monomer.
11. A sludge dehydrating agent of claim 1, to which is added an inorganic coagulant agent.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP93/00904

A. CLASSIFICATION OF SUBJECT MATTER	
Int. Cl ⁵ C02F11/14, B01D21/01	
According to International Patent Classification (IPC) or to both national classification and IPC	

B. FIELDS SEARCHED	
Minimum documentation searched (classification system followed by classification symbols)	
Int. Cl ⁵ C02F11/14, B01D21/01	

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched	
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)	

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, A, 2-78499 (Dai-Ichi Kogyo Seiyaku Co., Ltd.), March 19, 1990 (19. 03. 90), Claim; lines 6 to 12, lower left column, page 2 (Family: none)	1-5, 7-10
Y	JP, A, 2-78499 (Dai-Ichi Kogyo Seiyaku Co., Ltd.), March 19, 1990 (19. 03. 90), Claim; lines 6 to 12, lower left column, page 2 (Family: none)	1-11
Y	JP, A, 56-118798 (Kurita Water Industries Ltd.), September 17, 1981 (17. 09. 81), Claim (Family: none)	1-11
Y	JP, A, 62-49918 (Ichikawa Keori K.K.), March 4, 1987 (04. 03. 87), Claim; line 14, lower left column, page 2 to line 10, upper left column, page 3 (Family: none)	1-11

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "X" document of particular relevance; the claimed invention cannot be understood without reference to it; it may be considered to involve a step which the document is taken to teach
- "Y" document of particular relevance; the claimed invention cannot be considered to involve a step which the document is taken to teach, but the document is cited to understand the principle or theory underlying the invention
- "Z" document member of the same patent family

Date of the actual completion of the international search September 8, 1993 (08. 09. 93)	Date of mailing of the international search report October 12, 1993 (12. 10. 93)
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Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer: Telephone No.
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP93/00904

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, A, 62-289300 (Toagosei Chemical Industry Co., Ltd.), December 16, 1987 (16. 12. 87), Claim; line 13, upper left column to line 14, upper right column, page 3, lines 1, lower right column, page 3 to line 5, upper left column, page 4 (Family: none)	1-11
A	JP, A, 59-92099 (Kurita Water Industries Ltd.), May 28, 1984 (28. 05. 84), Claim; lines 1 to 5, upper left column, page 3	1-11